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Synthesis of Fullerooxazoles: Novel Reactions of [60]Fullerene with Nitriles Promoted by Ferric Perchlorate

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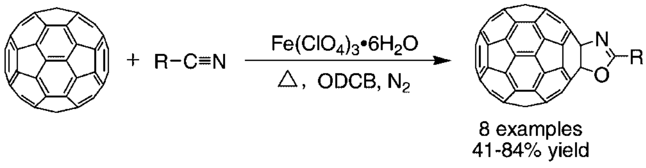

The ferric perchlorate-mediated reactions of C_{60} with various nitriles in *o*-dichlorobenzene under nitrogen atmosphere afforded the rare fullerooxazoles, which would be difficult to prepare by other methods. A possible reaction mechanism for the formation of the fullerooxazoles was proposed.

Many chemical reactions have been discovered for the functionalizations of fullerenes to prepare various fullerene products,[1] which may have promising applications in life science and materials science. Diverse types of organic molecules have been utilized as starting materials in fullerene chemistry. For example, the reactions of [60]fullerene (C_{60}) with various aldehyes[2] and ketones,[2,3] 1,3-dicarbonyl compounds such as malonate esters,[3a,4] β-keto esters,[3,5] and β-diketones,[3,5,6] and carboxylic acid derivatives such as carboxylic acids,[7] carboxylic anhydrides,[7b] and malonic acids[7b] give a diversity of fullerene products that incorporate with the desired different structural motifs. Although numerous reactants have been employed to the reactions with C_{60}, the reactions of nitriles with C_{60} have been seldom explored. Up to now, only a few works describing the reactions of C_{60} involving the cyano group were reported.[3a,4b,c,8] Bingel reported the reactions of bromomalononitrile and ethyl bromocyanoacetate with C_{60} in the presence of a base to afford methanofullerenes.[8a] Jagerovic et al. realized the synthesis of a C_{60}-fused tetrahydrofuran derivative by thermal reaction of C_{60} with tetracyanoethene oxide.[8b] We described the thermal reactions of 2-cyano-2-ethoxycarbonyl-3-aryloxiranes with C_{60} to give exclusively or predominantly cis isomers of C_{60}-fused tetrahydrofuran derivatives.[8c] We also reported the reactions of C_{60} with cyano-containing active methylene compounds to give methanofullerenes under solvent-free mechanical milling conditions in the presence of a base[3a] or mediated by $Mn(OAc)_3 \cdot 3H_2O$,[4b] as well as to afford an unsymmetrical 1,4-adduct generated from the radical reaction promoted by $Mn(OAc)_3 \cdot 3H_2O$.[4c] However, the direct reaction of C_{60} with the unsaturated carbon−nitrogen triple bond moiety of nitriles has not been reported to date.

Although a large variety of fullerene reactions have been explored extensively over the past two decades, the reactions of C_{60} promoted by metal salts are relatively scarce. Gan and co-workers reported the reactions of *tert*-butyl hydroperoxide with fullerenes catalyzed by metal salts such as $Ru(PPh_3)_3Cl_2$, $FeCl_3$, $Fe(NO_3)_3$, and $RuCl_3$ to produce the first fullerene mixed peroxides $C_{60}(O)(OO^tBu)_4$ and $C_{70}(OO^tBu)_{10}$.[9a] Shigemitsu et al. described the reactions of fullerene epoxides $C_{60}O_n$ ($n = 1$, 2) with benzaldehyde derivatives in the presence of *N*-(1-phenethyl)-2-cyanopyridinium hexafluoroantimonate to give fullerene acetals.[9b] Rubin and co-workers reported the synthesis of a novel compound with complete saturation of a single six-membered ring on fullerene C_{60} through a remarkable double 5-*exo*-trig addition of alkoxyl radicals promoted by $Pb(OAc)_4$.[9c] Troshina et al. described the $Pb(OAc)_4$-mediated oxidative coupling reactions of C_{60} with amino acid esters to obtain pyrrolidinofullerene derivatives.[9d] More recently, Itami's group reported the Ru-catalyzed arylation and alkenylation of C_{60} by organoboron compounds.[9e] Recently we have successfully applied $Mn(OAc)_3 \cdot 2H_2O$ to the reactions of C_{60} for the first time.[10] We reported the $Mn(OAc)_3 \cdot 2H_2O$-mediated reactions of C_{60} with various active methylene compounds, aromatic

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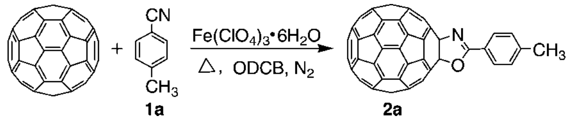
methyl ketones, β-enamino carbonyl compounds, and carboxylic acid derivatives affording singly bonded fullerene dimers,[4b] 1,4-adducts and 1,16-adduct of C_{60},[4b,c] C_{60}-fused dihydrofuran derivatives,[3b] methanofullerenes,[3b,4b] C_{60}-fused pyrroline derivatives,[11] and C_{60}-fused lactone derivatives.[7b] Interestingly, $Mn(OAc)_3 \cdot 2H_2O$ could also be employed to transform the in situ generated ArC_{60}-H into ArC_{60}-OAc in a one-pot procedure.[12] We also investigated the $Cu(OAc)_2 \cdot H_2O$-mediated reactions of C_{60} with ketonic compounds to afford the methanofullerenes and C_{60}-fused dihydrofuran derivatives.[3b]

In efforts to extend the reactions of C_{60} promoted by metal salts, we were determined to explore more metal oxidant-mediated reactions of C_{60}. To the best of our knowledge, the $Fe(ClO_4)_3 \cdot 6H_2O$-mediated reaction of C_{60} has not been reported until today. In continuation of our interest in fullerene chemesitry,[2b,3,4b,c,8c,10–13] herein we describe the $Fe(ClO_4)_3 \cdot 6H_2O$-promoted reactions of C_{60} with various nitriles to afford the scarce fullerooxazoles.

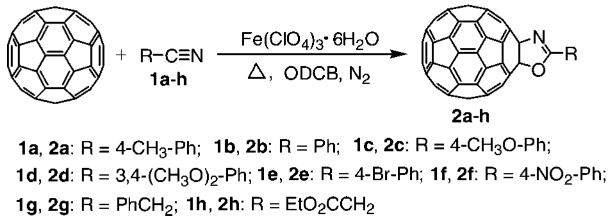
4-Tolunitrile (**1a**) was first chosen to react with C_{60} in the presence of $Fe(ClO_4)_3 \cdot 6H_2O$. At the onset, the mixture of $Fe(ClO_4)_3 \cdot 6H_2O$ (0.25 mmol) and 4-tolunitrile (5 mmol) was first dissolved in a chosen polar solvent (1 mL) such as dimethyl sulfoxide (DMSO) or *N*,*N*-dimethylformamide (DMF), then an *o*-dichlorobenzene (ODCB, 6 mL) solution of C_{60} (0.05 mmol) was added. The resulting solution was heated with vigorous stirring in an oil bath preset at 120 °C under nitrogen atmosphere for 5 h. To our disappointment, no obvious reaction was observed even in the presence of a large excess of 4-tolunitrile or by raising the reaction temperature and extending the reaction time. To successfully realize the $Fe(ClO_4)_3 \cdot 6H_2O$-mediated reaction of C_{60} with 4-tolunitrile, various reaction conditions have been examined. To our delight, the reaction was found to proceed well and gave fullerooxazole **2a** in 22% yield when the mixture of $Fe(ClO_4)_3 \cdot 6H_2O$ and 4-tolunitrile (1:100) was directly melted in an oil bath preset at 120 °C under nitrogen atmosphere, followed by the addition of the ODCB solution of C_{60}, and then the reaction mixture was heated with vigorous stirring under protection of nitrogen at 120 °C (entry 1, Table 1). Decreasing or increasing the reaction temperature did not improve the yield of product **2a** (entries 2 and 3, Table 1). Other reaction conditions for the reaction of C_{60} with 4-tolunitrile giving fullerooxazole **2a** were also examined. These results are summarized Table 1. No benefit to the yield of product **2a** could be achieved by variation of the amount of 4-tolunitrile (entries 4 and 5, Table 1). Similar results were obtained by increasing the amount of $Fe(ClO_4)_3 \cdot 6H_2O$ to 2 equiv (entries 6−8, Table 1). However, the reaction became much faster and thus easily out of control. Therefore, the reagent molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot 6H_2O$:**1a** as 1:1:100 and the reaction temperature as 120 °C were chosen as the optimized reaction conditions.

TABLE 1. Yields and Reaction Conditions for the $Fe(ClO_4)_3 \cdot 6H_2O$ (FEP)-Mediated Reaction of C_{60} with 4-Tolunitrile 1a



entry	molar ratio [C_{60}:FEP:**1**]	reaction temp (°C)	reaction time (min)	yield of **2a** (%)	recovered C_{60} (%)
1	1:1:100	120	15	22	51
2	1:1:100	100	30	19	66
3	1:1:100	140	5	19	53
4	1:1:50	120	10	14	53
5	1:1:200	120	30	19	68
6	1:2:50	120	5	19	41
7	1:2:100	120	5	23	54
8	1:2:200	120	8	23	47

SCHEME 1. $Fe(ClO_4)_3 \cdot 6H_2O$-Mediated Reactions of C_{60} with Nitriles 1a−h



With the optimized conditions in hand, this reaction was extended to other nitriles such as benzonitrile (**1b**), 4-methoxybenzonitrile (**1c**), 3,4-dimethoxybenzonitrile (**1d**), 4-bromobenzonitrile (**1e**), 4-nitrobenzonitrile (**1f**), phenylacetonitrile (**1g**), and ethyl cyanoacetate (**1h**), giving fullerooxazole derivatives **2b**,[14] **2c**,[14] **2d**, **2e**,[14] **2f**, **2g**, and **2h**, respectively (Scheme 1). The reaction conditions and yields for the $Fe(ClO_4)_3 \cdot 6H_2O$-promoted reactions of C_{60} with nitriles **1a**−**h** under nitrogen atmospheric conditions are summarized in Table 2.

As can be seen from Table 2, aromatic nitriles bearing either electron-withdrawing groups or electron-donating groups (**1a**−**f**) as well as aliphatic nitriles (**1g** and **1h**) could be successfully utilized to prepare fullerooxazoles. All of the examined nitriles **1a**−**h** gave fullerooxazoles **2a**−**h** in moderate to good yields, ranging from 41% to 84% based on consumed C_{60}. In the case of **1e** and **1f**, the prior addition of some amount of ODCB (1 mL) before the addition of C_{60} (dissolved in 6 mL of ODCB) to the molten mixture of $Fe(ClO_4)_3 \cdot 6H_2O$ with **1e** or **1f** successfully avoided the resolidification of the molten mixture because of higher melting points of nitriles **1e** and **1f** than other nitriles. It should be noted that for the reaction of C_{60} with ethyl cyanoacetate **1h**, some unknown byproducts were obtained besides the predominant product **2h**. Surprisingly, acetonitrile, the simplest aliphatic nitrile, did not react with C_{60} under the same conditions.

Products **2b**,[14] **2c**,[14] and **2e**[14] are known compounds, and their identities were confirmed by comparison of their spectral data with those reported in the literature. New compounds **2a**, **2d**, **2f**, **2g**, and **2h** were unambiguously characterized by their MS, ^{1}H NMR, ^{13}C NMR, FT-IR, and UV−vis spectra. All of the MALDI FT-ICR mass spectra of these fullerooxazole products

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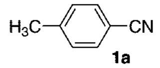
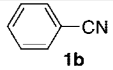
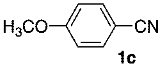
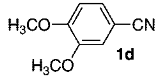
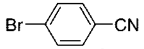
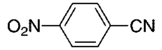
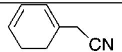
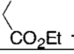
TABLE 2. Reaction Temperatures, Reaction Times, and Yields of Fullerooxazoles 2a−h and Recovered C_{60}[a]

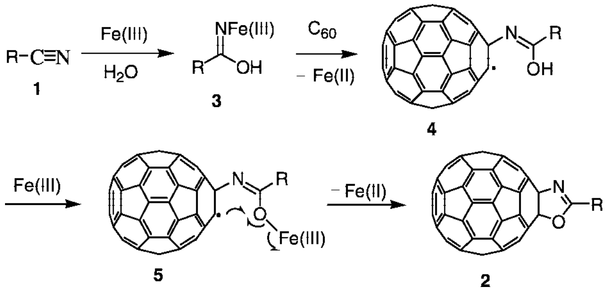
nitrile **1**	reaction temperature (°C)	reaction time (min)	yield of 2^b	recovered C_{60}
 **1a**	120	15	45%	51%
 **1b**	120	10	58%	64%
 **1c**	120	10	45%	62%
 **1d**	120	20	84%	81%
 **1e**	120	40^c	42%	67%
 **1f**	150	40^c	75%	88%
 **1g**	120	15	56%	75%
 **1h**	120	20	41%	51%

[a] Molar ratio of C_{60}:$Fe(ClO_4)_3 \cdot 6H_2O$:nitrile **1** = 1:1:100. [b] Yield based on consumed C_{60}. [c] After the mixture of $Fe(ClO_4)_3 \cdot 6H_2O$ with **1e** or **1f** was melted, ODCB (1 mL) was added at the molten temperature (above 140 °C for **1e** and above 170 °C for **1f**), followed by addition of the ODCB (6 mL) solution of C_{60} at the reaction temperature.

gave the correct molecular ion peaks. In the ^{13}C NMR spectra of compounds **2a**, **2d**, **2f**, **2g**, and **2h**, the peak for the C=N carbon appeared at 163.77−167.66 ppm, and the two sp^3-carbons of the C_{60} skeleton were located at 97.02−97.83 and 91.42−91.99 ppm, close to those of other fullerene derivatives, of which the oxygen atom[2b,7b,13d] and nitrogen atom[11] are connected to the C_{60} skeleton, respectively. No more than 29 peaks including some overlapped ones for the 58 sp^2-carbons of the C_{60} moiety were observed in the range of 135.60−148.94 ppm, consistent with the C_s symmetry of their molecular structures. The IR spectra of **2a**, **2d**, **2f**, **2g**, and **2h** showed absorptions at 1638−1663 cm^{-1} due to the C=N group. Their UV−vis spectra exhibited a peak at 413−416 nm, which is a diagnostic absorption for the 1,2-adduct of C_{60}, to which the oxygen atom is directly attached.[7b]

Fullerooxazoles were previously prepared by two steps, that is, photochemical reactions of C_{60} with arylazides[14] or thermal reactions with azidoformates and hydroxamic acid derivatives,[15] followed by rearrangement of the formed fulleroaziridines to fullerooxazoles. Our current one-step approach to the synthesis of fullerooxazoles from cheap and easily available nitriles and $Fe(ClO_4)_3 \cdot 6H_2O$ is obviously more straightforward and practical than the previous protocols.[14,15]

SCHEME 2. Proposed Reaction Mechanism for the Formation of Fullerooxazoles



On the basis of the previously suggested mechanisms for the radical reactions of C_{60} promoted by $Mn(OAc)_3 \cdot 2H_2O$[3b,5b,11] and $Cu(OAc)_2 \cdot H_2O$,[3b] together with the reaction mechanism for the ferric perchlorate-mediated oxidative additions[16] of olefins with substituted diethyl α-benzylmalonates or diethyl (pyridylmethy1)malonates, we propose a possible reaction mechanism for the formation of fullerooxazoles **2a**−**h** from the $Fe(ClO_4)_3 \cdot 6H_2O$-mediated reactions of C_{60} with nitriles **1a**−**h**, as shown in Scheme 2. The additions of nucleophiles including water to metal-activated organonitriles have been reported.[17] Similarly, nitrile **1** reacts with one molecule of H_2O in the presence of $Fe(ClO_4)_3 \cdot 6H_2O$ to generate Fe(III)-complex **3**, which is consistent with the reddening of the molten mixtures from nitriles and $Fe(ClO_4)_3 \cdot 6H_2O$, indicating the formation of complexes between Fe(III) and nitriles.[16b] Homolytical addition of **3** to C_{60} produces fullerenyl radical **4**, followed by coordination with another molecule of $Fe(ClO_4)_3 \cdot 6H_2O$ to generate Fe(III)-complex **5** and subsequent intramolecular cyclization with the loss of Fe(II) species to afford fullerooxazole derivatives **2a**−**h**. Alternatively, fullerenyl radical **4** could be oxidized to the corresponding fullerenyl cation, followed by cyclization with the loss of H^+ to give the fullerooxazole derivatives. The addition of water to nitrile **1** affording intermediate **3** would be facilitated with an electron-withdrawing R group. This proposed reaction mechanism could reasonably explain the failed reaction with acetonitrile due to the electron-donating property of the methyl group.

In summary, $Fe(ClO_4)_3 \cdot 6H_2O$ has been successfully utilized in the free radical reactions of C_{60} for the first time. The reactions of C_{60} with nitriles in the presence of $Fe(ClO_4)_3 \cdot 6H_2O$ afforded the scarce fullerooxazole derivatives.[18] The direct melting of nitriles and $Fe(ClO_4)_3 \cdot 6H_2O$ proved to be crucial for the successful realization of the reaction. The current method provided a facile one-step route for the synthesis of fullerooxazoles. A plausible reaction mechanism for the formation of fullerooxazoles was proposed.

Experimental Section

Preparation of Fullerooxazoles 2a−h. A mixture of nitrile **1a** (**1b**, **1c**, **1d**, **1e**, **1f**, **1g**, or **1h**, 5 mmol) and ferric perchlorate hexahydrate (23.0 mg, 0.05 mmol) was melted in an oil bath preset at 120 °C in a 50-mL round-bottomed flask equipped with a reflux condenser, nitrogen inlet and outlet, and a magnetic stirrer, then C_{60} (36.0 mg, 0.05 mmol, dissolved in 7 mL of *o*-dichlorobenzene) was added and the resulting solution was heated with vigorous stirring at 120 °C under nitrogen atmosphere. The reaction was monitored by TLC and stopped at the designated time. The reaction

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(18) After our work had been completed, an independent work on the reaction of electrochemically generated C_{60} anion in benzonitrile to afford fullerooxazole product **2b** was published: Zheng, M.; Li, F.-F.; Ni, L.; Yang, W. W.; Gao, X. *J. Org. Chem.* **2008**, *73*, 3159.

mixture was passed through a silica gel plug to remove any insoluble material. After the solvent was evaporated in vacuo, the residue was separated on a silica gel column with carbon disulfide/toluene as the eluent to give unreacted C_{60} and fullerooxazole.

2a: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.37 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 2.57 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 165.38 (1C), 147.82 (1C), 147.66, 147.41 (1C), 146.00, 145.98, 145.86, 145.70, 145.65, 145.38, 145.22, 145.09, 144.83, 144.72, 144.45, 144.19, 143.88, 143.30, 142.75 (1C, aryl *C*), 142.39, 142.36, 142.29, 141.95 (4C), 141.87, 141.73, 141.61, 141.58, 140.01, 139.22, 137.51, 135.88, 129.22 (aryl *C*), 128.97 (aryl *C*), 123.66 (1C, aryl *C*), 97.02 (1C, sp^3-*C* of C_{60}), 91.77 (1C, sp^3-*C* of C_{60}), 21.62 (1C); FT-IR ν/cm^{-1} (KBr) 2919, 2850, 1639, 1510, 1427, 1321, 1179, 1141, 1087, 1023, 983, 932, 824, 720, 660, 603, 562, 525; UV−vis (CHCl$_3$) λ_{max}/nm (log ϵ) 257 (5.17), 315 (4.68), 414 (3.55), 687 (2.42); MALDI FT-ICR MS *m/z* calcd for $C_{68}H_7NO$ [M$^-$] 853.05276, found 853.05277.

2d: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ7.99 (dd, J = 8.3, 1.6 Hz, 1H), 7.90 (d, J = 1.6 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 4.02 (s, 3H), 3.99 (s, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 164.99 (1C), 152.61 (1C, aryl *C*), 148.94 (1C), 147.98, 147.94 (1C), 147.53 (1C), 146.13, 146.10, 145.98, 145.83, 145.78, 145.49, 145.31, 145.21, 144.96, 144.84, 144.57, 144.34, 144.02, 143.54, 142.53, 142.50, 142.43, 142.11 (4C), 142.01, 141.86, 141.75 (4C), 140.17, 139.34, 137.64, 135.93, 122.87 (1C, aryl *C*), 119.10 (1C, aryl *C*), 111.66 (1C, aryl *C*), 110.69 (1C, aryl *C*), 97.15 (1C, sp^3-*C* of C_{60}), 91.94 (1C, sp^3-*C* of C_{60}), 55.71 (1C), 55.62 (1C); FT-IR ν/cm^{-1} (KBr) 2924, 2850, 1638, 1512, 1458, 1423, 1315, 1272, 1227, 1177, 1139, 1092, 1025, 986, 938, 871, 810, 770, 705, 569, 526; UV−vis (CHCl$_3$) λ_{max}/nm (log ϵ) 257 (5.11), 314 (4.74), 413 (3.62), 682 (2.42); MALDI FT-ICR MS *m/z* calcd for $C_{69}H_9NO_3$ [M$^-$] 899.05824, found 899.05574.

2f: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 8.66 (d, J = 8.7 Hz, 2H), 8.48 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 163.77 (1C), 150.03 (1C, aryl *C*), 148.08 (1C), 147.66 (1C), 146.96, 146.28 (4C), 146.14, 145.98, 145.93, 145.69, 145.27, 145.19, 145.10, 145.00, 144.45, 144.38, 144.07, 142.83 (1C, aryl *C*), 142.69, 142.62 (6C), 142.20, 142.11, 142.06, 141.99, 141.85, 141.71, 140.36, 139.55, 137.64, 136.06, 130.06 (aryl *C*), 123.75 (aryl *C*), 97.83 (1C, sp^3-*C* of C_{60}), 91.99 (1C, sp^3-*C* of C_{60}); FT-IR ν/cm^{-1} (KBr) 2920, 2851, 1645, 1598, 1522, 1461, 1430, 1345, 1320, 1090, 1020, 982, 929, 864, 850, 702, 526; UV−vis (CHCl$_3$) λ_{max}/nm (log ϵ) 255 (5.05), 316 (4.65), 416 (3.51), 689 (2.27); MALDI FT-ICR MS *m/z* calcd for $C_{67}H_4N_2O_3$ [M$^-$] 884.02219, found 884.02167.

2g: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.2 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 4.22 (s, 2H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 167.66 (1C), 147.68 (1C), 147.28, 145.86 (5C), 145.74, 145.58, 145.54, 145.26, 145.03, 144.95, 144.71, 144.60, 144.26, 144.05, 143.74, 142.88, 142.28, 142.24, 142.17, 141.84, 141.75 (4C), 141.59, 141.48, 141.42, 139.90, 139.11, 137.22, 135.60, 133.82 (1C, aryl *C*), 128.80 (aryl *C*), 128.58 (aryl *C*), 127.14 (1C, aryl *C*), 97.09 (1C, sp^3-*C* of C_{60}), 91.48 (1C, sp^3-*C* of C_{60}), 34.82 (1C); FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1658, 1493, 1452, 1425, 1267, 1213, 1178, 1131, 1060, 980, 937, 721, 695, 600, 574, 526; UV−vis (CHCl$_3$) λ_{max}/nm (log ϵ) 256 (5.05), 316 (4.56), 414 (3.47), 683 (2.38); MALDI FT-ICR MS *m/z* calcd for $C_{68}H_7NO$ [M$^-$] 853.05276, found 853.05298.

2h: ^{1}H NMR (300 MHz, $CS_2/CDCl_3$) δ 4.38 (q, J = 7.1 Hz, 2H), 3.98 (s, 2H), 1.44 (t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CS_2/CDCl_3$ with Cr(acac)$_3$ as relaxation reagent) (all 2C unless indicated) δ 165.64 (1C), 163.12 (1C), 147.78 (1C), 147.37 (1C), 146.94, 145.97 (4C), 145.85, 145.68, 145.63, 145.38, 145.06, 145.03, 144.81, 144.71, 144.31, 144.12, 143.82, 142.65, 142.38, 142.33, 142.27, 141.94, 141.84, 141.81, 141.69, 141.56, 141.49, 139.99, 139.23, 137.34, 135.76, 97.42 (1C, sp^3-*C* of C_{60}), 91.42 (1C, sp^3-*C* of C_{60}), 61.59 (1C), 34.82 (1C), 14.11 (1C); FT-IR ν/cm^{-1} (KBr) 2922, 2852, 1744, 1663, 1550, 1532, 1462, 1433, 1369, 1269, 1183, 1031, 982, 942, 605, 527; UV−vis (CHCl$_3$) λ_{max}/nm (log ϵ) 255 (5.09), 316 (4.61), 414 (3.63), 687 (2.46); MALDI FT-ICR MS *m/z* calcd for $C_{65}H_7NO_3$ [M$^-$] 849.04259, found 849.04247.

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Supporting Information Available: ^{1}H NMR spectra of **2a**−**h** as well as ^{13}C NMR spectra of **2a**, **2b**, **2d**, **2f**, **2g**, and **2h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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